



RESEARCH

Modeling the Fate of Oil Spills at Sea

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A numerical model for the simulation of the physicochemical weathering processes of an oil spill at sea is presented based on state-of-the-art models. The model includes the most significant processes: spreading, evaporation, dispersion into the water column, emulsification and the change in viscosity and density. These processes depend on each other and are allowed to vary simultaneously since processes are described by a set of differential equations, solved by a fourth-order Runge-Kutta method. Numerical examples are given, in order to test the results obtained, and compared with available experimental data in the literature. The model predicts well the variation of water incorporation, density and viscosity but seems to overestimate the fraction evaporated. However more experimental data are needed to calibrate and validate the model since differences in the composition of the simulated oil and the samples from which experimental data are taken may occur in evaporation studies. The model is suitable to join other modules for the prediction of the spill trajectory by advection due to winds and currents and sub-sea transport. Copyright © 1996 Elsevier Science Ltd

Oil pollution at sea has been receiving particular attention over the past years by scientists and governments as the consequence of a number of serious accidents involving the release of large amounts of oil at sea. Two examples can be mentioned: the *Torrey Canyon* oil spill in 1967, a 296 m tanker, which ran aground off the southwest coast of England, releasing approximately 100 000 t (134.5 ML) of Kuwait crude, and more recently, the *Exxon Valdez* oil spill in 1989, which spilled 11.2 million gallons (42.4 ML) of crude oil in Alaska.

Oil enters the marine environment in many ways, including natural seeps. Natural seeps represent the largest part of the total oil entering the sea (National Research Council, 1985), but it is the oil released in consequence of the human activity such as refinery emissions, ship cleaning operations, well blow-outs and accidental spills which have the potential to cause significant impact on the marine environment. In particular, tanker accidents which may result in the discharge of relatively large quantities of oil near to sensitive coastal marine environments, are of great concern.

Response measures to an oil spill are enhanced by the capability to forecast the short-term and long-

term behaviour of the spilled oil. To implement an effective response it is important, not only to be able to track the spilled oil but also to know the oil's condition; it may be too thin to skim or too viscous to disperse (Mackay & McAuliffe, 1988).

Considerable amounts of work have been directed towards understanding and quantifying the spill processes, in order to develop spill models able to predict the trajectory and fate of spilled oil. These models have three major modules: an input module of oil and environmental data, a calculation module using trajectory and fates algorithms that describe the processes involved and an output model which presents the required results in a suitable way.

The fate of oil at sea is determined by several physicochemical properties of the oil as well as by the environmental conditions. While the latter are site and time dependent, the former depend basically on the chemical properties of the crude oil. This paper will concentrate mainly on the models that predict the fate of an oil spill in calm weather and without the influence of waves and water currents. It is recognized that the sea state conditions have an important influence on the behaviour of spilled oil, but waves and water currents involve different types of mechan-

isms which are not taken into consideration in this paper.

The main mechanisms which govern the fate of an oil slick at sea are spreading, evaporation, dispersion, emulsification, sedimentation and biodegradation. They are understood with different levels of confidence and can be described by mathematical models partially based and calibrated on empirical results. The nature of the different mechanisms will be reviewed and an overall algorithm is proposed to predict their combined effect on the fate of oil spills at sea.

Mechanisms of the Physical-Chemical Weathering Processes

In this section some of the available algorithms describing physical and chemical weathering processes are described. Each process is described individually, making use of available physical and environmental data (e.g. wind speed, temperature, oil composition). The coupling of the different algorithms must reflect the fact that the processes are occurring simultaneously and that they interact with each other (e.g. if oil enters the water column, the surface evaporation rate will decrease).

Spreading mechanism

Spreading of low pour point oil released on water is probably the most dominant process in the first stage of a spill. Since spreading strongly influences later processes such as evaporation and dispersion, it is logical to discuss this process first.

When oils come in contact with water they rapidly reach water temperature, which may be below that of the pour point of waxy oils. Thus a pre-requisite for spreading of a particular crude oil or refined product after spillage is that its pour point must be lower than the ambient seawater temperature. Crude oils with high wax content or refined products are characterized by a high pour point and these materials will easily solidify either immediately or shortly after spillage at sea. Formation of wax crystal matrices in oil also reduces the ability of the oil to disperse naturally as small droplets in the ocean, hence the formation often of sizable floating tar balls. As a first attempt to classify different crude oils with respect to their behaviour at sea, a characterization by wax content (and pour point) seems feasible, as proposed in CONCAWE (1983).

Many oils spilled on the surface of calm water will spread in the form of a thin continuous layer with a circular pattern as a result of gravity and net surface tension. The *net surface tension*, or *spreading coefficient* is the difference between the air/water surface

tension and the sum of the air/oil surface tension and the oil/water interfacial tension. Although viscosity does have some effect on the rate of spreading, particularly shortly after spillage, many oils tend to spread on a water surface at about the same rate even though they may possess different viscosities. The dominant physicochemical parameters of the crude oil that determine spreading are thus in addition to its pour point, its density and its spreading coefficient.

The spreading behaviour of two crude oils with almost comparable spreading coefficients but with a considerable difference in density (e.g. Ekofisk and Tia Juana Pesado) is very similar, showing only a difference in areas, in the first few hours, at most by a factor of 2.

The rate of spreading of different crude oils with spreading coefficients of 10 and 30 mN m⁻¹ respectively, and similar density, may differ at most by a factor of 3 (CONCAWE, 1983).

The influence of spill volume on spreading rate, is as shown in CONCAWE, 1983, that with larger spills, the change from the one spreading phase to the other occurs after longer periods of time.

The most widely used spreading model is the one developed by Fay (1969). In the spreading process Fay distinguishes three phases each one being determined by the dominant spreading and retarding forces involved. The first phase is the gravity-inertial spreading which lasts only a few minutes except for large spills. The third phase, the tension-viscous phase, occurs when the slick may be dispersed or broken into separate slicks. So it is common that spill models consider mainly the second phase, known as the gravity-viscous spreading, for the simulation of spreading. The formula for the second phase is according to Fay's model as modified by Wang *et al.* (1975):

$$A_2 = \pi 0.98^2 \left[\frac{\Delta \rho g V^2}{\rho_w \nu_w^{1/2}} \right]^{1/3} t^{1/2} \quad (1)$$

where A_2 = area of slick (m²)
 g = acceleration of gravity (ms⁻²)
 V = volume of spill (m³)
 t = time (s)
 ρ_w = seawater density
 $\Delta \rho$ = density difference between seawater and oil
 ν_w = kinematic viscosity of seawater (m² s⁻¹)

Because Fay's formula(s) greatly underestimates the slick growth, Lehr *et al.* (1984) developed a Fay-type

formula which is suitable to estimate initial spill size given the observed spill area.

$$A = 2270 \left[\frac{\Delta\rho}{\rho_0} \right]^{2/3} V^{2/3} t^{1/2} + 40 \left[\frac{\Delta\rho}{\rho_0} \right]^{1/3} V^{1/3} W^{4/3} t \quad (2)$$

where A = area of slick (m^2)
 W = wind speed (Knot)
 V = volume of spill (barrel)
 t = time (min)
 ρ_0 = oil density
 $\Delta\rho$ = density difference between water and oil

This formula computes total slick area (spreading is reported to be separated in two major regimes: a thick 'black oil' regime and thin 'sheen' regime (Lehr *et al.*, 1984)).

The rate of change of surface area used by some authors (Reed, 1989; Spaulding *et al.*, 1992) which is based on the gravity-viscous formulation of Fay (1969) and Hoult (1972) as modified by Mackay *et al.* (1980) is useful for oil spill models that have many variables changing simultaneously. The rate of spreading is calculated by

$$\frac{dA}{dt} = K_1 A^{1/3} \left[\frac{V_m}{A} \right]^{4/3} \quad (3)$$

where A = area of slick (m^2)
 K_1 = constant with default value of 150 s^{-1} (Mackay *et al.*, 1980)
 V_m = volume of spill (m^3)
 t = time (s)

Evaporation

Evaporation is the primary initial process involved in the removal of oil from sea. The rate of evaporation is determined by the physicochemical properties of the oil and is increased by spreading, high water temperatures, strong winds and rough seas. By evaporation, low boiling components will rapidly be removed, thus reducing the volume of the remaining slick. Evaporation from the surface slick is for many oils the most important mass loss processes during the first hours of an oil spill.

The rate of evaporation of lighter components is influenced by the percentage of lighter components in the crude oil itself, the oil temperature, the oil thickness and area, and the physical forces of wind and wave energy.

The volatility characteristics of the crudes may be described by the respective distillation curves representing the temperature, at atmospheric pressure, corresponding to a volume or weight fraction which can be removed by distillation up to that temperature.

For larger spill volumes the rate of evaporation decreases since the surface area/volume ratio of the slick for larger spills decreases, i.e. the slick thickness increases. As expected the rate of evaporation increases with increasing temperature and wind speed. However, this effect is relatively small as can be seen in Figs 1 and 2.

As a consequence of removal of the lighter hydrocarbons through evaporation, producing a reduction in the volume, the density and viscosity increase. The change of these parameters is important with respect to processes such as natural dispersion, emulsification, dissolution and sinking of the oil.

It is possible to estimate the density and the viscosity of the remaining oil after evaporation, using spreading and evaporation models to calculate the volume fraction evaporated under ambient conditions. However the effect of emulsification must be included since it affects density significantly.

During the first 24 h after spillage, most crude oils will have lost most of their lighter components, which represent approximately 25–30% of the total crude oil and, although the loss continues, the rapid evaporative process can be assumed to have ended.

Two methods are currently used to compute evaporation rate: the pseudo-component approach and

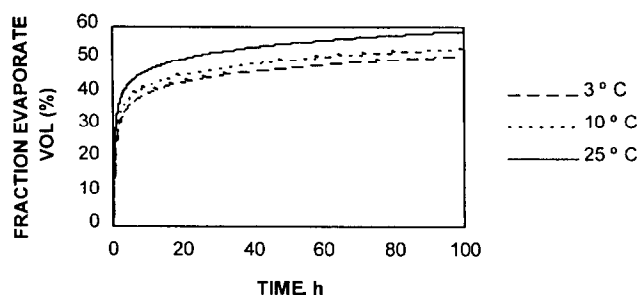


Fig. 1 Effect of temperature on evaporation curves, for a Kuwait crude oil spill of $10,000 \text{ m}^3$ at a wind speed of 8 knots..

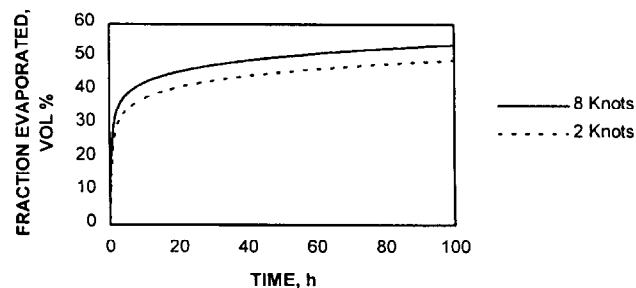


Fig. 2 Effect of wind speed on evaporation curves for a Kuwait crude oil spill of $10,000 \text{ m}^3$ at a temperature of 10°C .

the analytic approach (Spaulding, 1988). In the pseudo-component approach oil, is characterized by a set of hydrocarbon components grouped by molecular weight or by boiling point fraction (Reed, 1989). This allows different fractions of the oil to evaporate at different rates depending on the fraction considered. The mass transfer rate is given by

$$\frac{dm_i}{dt} = \frac{K_2 P_i A f_i M_i}{RT} \quad (4)$$

where m_i = mass of i^{th} constituent
 t = time (s)
 P_i = vapor pressure (atm)
 A = spill area (m^2)
 f_i = fraction of spill which is constituent i
 M_i = molecular weight (g mol^{-1})
 R = gas constant ($8.206 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1} \text{ K}^{-1}$)
 T = temperature (K)

The coefficient K_2 is the mass transfer coefficient given by Mackay & Matsugu (1973) as:

$$K_2 = 0.029 W^{0.78} D^{-0.11} S^{-0.67} \quad (5)$$

where K_2 = mass transfer coefficient for evaporation (m s^{-1})
 W = wind speed (m h^{-1})
 D = spill diameter (m)
 S_c = Schmidt number
 M_i = molecular weight of volatile portion of spill (g mol^{-1})

The Schmidt number usually used is 2.7 which is the Schmidt number value for cumene (Reed, 1989, Spaulding *et al.*, 1992, etc.).

Buchanan & Hurford (1988) group(s) the spill diameter, the Schmidt number and the numerical value in equation (5) in one constant and calculate(s) the mass transfer coefficient as:

$$K_2 = 2.5 \times 10^{-3} W^{0.78} \quad (6)$$

In the analytic approach, vapor pressure is computed as a function of the temperature and the amount evaporated. An example of an analytic approach was presented by Drivas (1982, 1983) and commented by Feigley (1983) who derived expression (7) for the calculation of evaporation rates of individual compounds and the total emission rate from an oil spill, provided the individual vapor pressures of pure oil constituents, initial mole fraction of each one and, if more accuracy is desired, the activity coefficients.

$$\frac{dm}{dt} = -k m_T^0 \frac{\sum_{i=1}^N [X_i^0 \gamma_i p_i^s M_i e^{-k \gamma_i P_i^s t}]}{\sum_{i=1}^N [x_i^0 M_i]} \quad (7)$$

where m_T^0 = total initial mass of evaporable liquid
 t = time (s)
 N = number of components
 x_i^0 = initial liquid mole fraction of component i
 γ_i = activity coefficient of component i
 M_i = molecular weight of component i
 p_i^s = saturation vapor pressure of component i

and k is given by

$$k = \frac{K_2 A}{R T n_T} \quad (8)$$

where n_T is the total liquid moles.

Equation (7) needs a lot of information, namely oil composition, vapor pressure and activity coefficients (if available) of each evaporable component.

Another approach that is being used by some authors (Buchanan & Hurford, 1988; Anderson *et al.*, 1993) relates fraction evaporated to a dimensionless group termed Θ , the evaporative exposure, and Henry's law constant, was derived by Stiver & Mackay (1984). The evaporation loss as a function of time elapsed is given by

$$F_E = \frac{T}{BT_G} \ln \left[\frac{BT_G}{T} \frac{K_2 t}{H} \exp \left(A - \frac{BT_0}{T} \right) + 1 \right] \quad (9)$$

$$\Theta = \frac{K_2 t}{h} \quad (10)$$

where: F_E = fraction evaporated
 T = temperature (K)
 T_0, T_G, A, B = constants derived from distillation data
 t = time (s)
 K_2 = mass transfer coefficient for evaporation (m s^{-1})
 h = slick thickness

In this approach only the constants T_0 , T_G , A and B which result from distillation data are needed to calculate the fraction evaporated. If evaporative exposure is used, direct comparison of different crude oils is allowed independent of environmental conditions.

Emulsification

Emulsification of crude oils and/or refined products involves the dispersion of water droplets into the oil medium. With respect to the potential for emulsification of an oil and emulsion stability, it is generally agreed that a critical factor is the amount of natural surfactant present in the spilled oil.

Although light oils (even gasoline or kerosene) will form emulsions, they are relatively unstable and they will settle out under calm conditions. The ability of crude oil to emulsify seems to be related to the level of asphaltenes in the oil, and the stability of emulsion is considered to be related to the presence of wax crystals. A crude oil with a relatively low asphaltene content is expected to be less likely to form a stable emulsion. However, stable emulsions are also associated with high wax contents (high pour points) (CONCAWE, 1983).

The result of emulsification is not only a large increase in volume (3 or 4 times the volume of the original stabilized oil) but also a significant increase in the density and a very large increase in viscosity.

The incorporation of water into oil may be computed by equation (11) derived by Mackay *et al.* (1980).

$$Y = C_3 \left[1 - \exp \left(\frac{-2 \times 10^{-6}}{C_3} (1 + W)^2 t \right) \right] \quad (11)$$

where Y = fractional water content

C_3 = mousse viscosity constant (final fraction water content) ~ 0.7 for crude oils and heavy fuel oil, and 0.25 for home heating oil.

W = wind speed (m s^{-1})

Mousse formation causes an increase in viscosity which may be computed by the Mooney equation:

$$\mu = \mu_0 \exp \left[\frac{2.5Y}{(1 - C_3 Y)} \right] \quad (12)$$

where μ_0 = parent oil viscosity (cP). Buchanan & Hurford (1988) calculates the parent oil viscosity by $\mu_0 = 224 A^{1/2}$ where A = asphaltene content (%).

Evaporation also causes an increase in viscosity which may be computed by equation (13).

$$\mu = \mu_0 \exp [C_4 F_E] \quad (13)$$

where C_4 = oil dependent constant that varies between about 1 and 10 where; 1 is for gasoline, or light diesel; and 10 for crude oils (Mackay *et al.*, 1980)

F_E = fraction of oil evaporated

If the viscosity of a crude has been measured at a different temperature, recalculation to a standard temperature will be necessary. The relationship between the viscosity of the remaining oil after distillation (presented as $\log v$) and the volume fraction distilled, can be described by a linear curve with constant slope, although some exceptions do exist.

Like viscosity, density increases are the consequence of both evaporation and mousse formation. Density increase may be calculated by (Buchanan & Hurford, 1988):

$$\rho_e = Y\rho_w + (1 - Y)(\rho_c + C_3 F_E) \quad (14)$$

where ρ_e = emulsion density (kg m^{-3})

ρ_w = density of seawater (kg m^{-3})

ρ_c = density of original crude oil (kg m^{-3})

Y = fraction of water content

Effect of wind, current and wave field

The theoretical model assumes that oil spreads to form a circular slick of uniform thickness. In practice, spilt oil is subject to the action of wind and water movement. The wind elongates the slick and the action of both wind and water movement breaks up the slick into windrows of thicker layers of oil aligned in the direction of the prevailing wind with areas of sheen or open water between windrows. This results in slicks extending for several kilometers in length but of only a few hundred meters in width. The total slick area may, however, approximate to the area of the theoretical slick. Within this slick, the oil is unevenly spread and its thickness varies considerably.

Advection of oil is also a result of wind, current and wave field. Most models use one or a combination of three methods to generate wind fields (Spaulding, 1988): 1) random walk process, 2) Markov chain process, or 3) meteorological models. The current field is generally calculated as the vectorial sum of wind, tidal, density and pressure gradient induced currents. Very often the residual current is small and may be neglected in many calculations, particularly in open seas where oil will be moved mainly by the action of wind.

The wind-induced drift component which is often the most important factor determining surface oil slick trajectory, is assumed to be approximately 2–4% of wind speed (Spaulding (1988), Mackay & McAuliffe (1988)) although a value of 3% is used for most calculations. A Coriolis force correction is sometimes introduced. The drift angle caused by wind is commonly assumed to be between 0 and 20° , typically

10–17° (Spaulding (1988)) although a variable angle depending on wind speed may be considered.

Entrainment of oil to the water column

Natural dispersion of crude oils and/or refined products after spillage at sea is the process of forming small droplets of oil which will be incorporated in the water column. Besides evaporation, the rate of natural dispersion largely determines the life of an oil slick on the sea surface. In practice natural dispersion can be significant and account for a major part of removal of oil from the sea surface.

Natural dispersion reduces the volume of slick at surface and reduces the evaporative loss, but it does not lead to changes in the physicochemical properties of the spilled material in the way that evaporation, for example does. In general, oil-in-water emulsions are not stable, and oil droplets may coalesce and return to the surface, as the reformed slick, particularly under very calm sea state conditions when dispersion of the oil droplets into the body of the sea, is not favoured.

Natural dispersion is still a poorly understood process, and the mathematical description of it is still in development phase. Studies indicate that natural dispersion is the net result of three separate processes, viz., the initial process of globulation which is the formation of oil droplets from slick under influence of breaking waves, the process of dispersion which is the transport of the oil droplets into the water column as a net result of the kinetic energy of oil droplets supplied by the breaking waves and the rising forces, and the process of coalescence of the oil droplets with the slick (CONCAWE, 1983).

Another most important parameter influencing natural dispersion is the oil/water interfacial tension, which only affects globulation and coalescence, and not the transport (dispersion) of oil droplets into the water column. The density and viscosity of the spilt material also affect natural dispersion. The more viscous the oil is, the lower its ability to form oil droplets.

Reed (1989) uses an approach which is based on the (a) formulation by Mackay *et al.* (1980) to compute entrainment or dispersion of surface oil into the water column. The fraction of sea surface oil dispersed or entrained into the water column is calculated as a lost fraction of sea surface oil per hour given by

$$D = D_a D_b \quad (15)$$

where D_a , the fraction of sea surface dispersed per hour, and D_b , the fraction of dispersed oil not returning to the slick are expressed by:

$$D_a = 0.11(W + 1)^2 \quad (16)$$

$$D_b = (1 + 50\mu^{1/2}\delta s_t)^{-1} \quad (17)$$

where W = wind speed (m/s)
 μ = viscosity (cP)
 δ = slick thickness (cm)
 s_t = oil–water interfacial tension (dyne cm⁻¹)

A new important development in oil spill modeling consists in characterizing oil as a distribution of droplets that form and penetrate the water column due to breaking waves. Submerged oil parcels (submerged spill) also break up into droplets due to turbulence in ambient water. In some spills (e.g. Braer oil spill) an important way of oil transportation was reported to be subsurface dispersed oil which by interaction with sediments, caused a deposition of 15% of the oil on the sea bed in a location not predicted by the simulation (Procter *et al.*, 1994; Turrel, 1994). The possibility that subsurface oil droplets may interact with particulates suspended in the water column, highlights the importance for fully three-dimensional oil spill models to be developed.

Using the model developed by Delvigne & Sweeney (1988), the entrainment rate is computed by

$$Q_r(d_0) = C(o) D_{ba}^{0.57} S F d_0^{0.7} \Delta d \quad (18)$$

where $Q_r(d_0)$ = entrainment rate of oil droplets with droplet sizes in an interval Δd around d_0 per unit surface area (kg m⁻² s⁻¹)
 $C(o)$ = empirical entrainment constant which depends on oil type and weathered state
 D_{ba} = dissipated breaking wave energy per unit surface area (J m⁻²)
 S = fraction of sea surface covered by oil ($0 \leq S \leq 1$)
 F = fraction of sea surface hit by breaking waves (white caps) per unit time (s⁻¹)
 d_0 = oil particle diameter (m). The oil droplet size range typically varies from 2–1600 μ m with most of the oil volume in the 50–300 μ m droplet size range
 Δd = oil particle diameter interval (m)

The dissipated breaking wave energy is given by the semi-empirical relation

$$D_{ba} \sim 0.0034 \rho_w g H_{rms}^2 \quad (19)$$

where H_{rms} = r.m.s. value of wave height in the wave field

ρ_w = density of seawater (kg m^{-3})

g = acceleration due to gravity (m s^{-2})

Overall appraisal

Most reviews on oil spill modeling (e.g. Krogh, 1984, Spaulding, 1988, Mackay & McAuliffe, 1988) present a list of the dominant oil spill processes with reference to the state of understanding of phenomena and existence of describing algorithms. Those processes are summarized in Table 1 with a short description of their relative importance, dominant operative time and the variables they depend on. Table 1 also contains the qualitative scale of present understanding and ability to write descriptive equations, as presented by Mackay & McAuliffe (1988).

Table 1 is completed by shoreline interactions (G/F) and ice interactions (F/P). The environment surrounding the oil spilled determines the algorithms used in each case since the fate of oil differs whether spill occurs at open sea, or contacts a coastal zone.

Modeling the Fate of Oil Spills

Problem formulation

When oil is spilled at sea, all the processes previously considered in this paper, occur simultaneously. In order to allow variables that depend on each other to vary simultaneously, processes must be described by a system of differential equations, which can be solved by numerical integration. This approach also allows environmental variables, such as wind speed, to be changed along the simulation.

This formulation concerns the surface slick alone rather than the other components (air, water column or sea floor). The goal is to model the fate of surface

Table 1 Summary of the dominant oil spill processes

Process	Importance	Dominant operative time	Dependence	Understanding/ability to write equations*
Spreading	area extent		gravity, surface tension, inertia, viscosity and/or droplet size distribution, shear diffusion.	F/F
Drifting	passage over larger areas/volumes of water		wind and water currents	G/G
Evaporation	loss of 20–40% (mass); it increases density and viscosity	first few hours	spill area, slick thickness, oil vap. pressure (a function of oil composition and temperature), mass transfer coefficient (primarily a function of wind speed).	E/G
Dissolution	loss of ~1% (mass); it may be important from toxicological viewpoint	shortly after spill	dissolution mass transfer coefficient (low), solubility (small in water (presence of soluble hydrocarbons)	E/F
Dispersion (oil-in-water emulsions)	from 10–15 $\mu\text{g l}^{-1}$ up to 1–2 mg l^{-1} in the top 10 meters of water column		sea state (wind shear and breaking waves)	P/VP
Emulsification (water-in-oil emulsions)	uptake of up to 80% water into oil; increases viscosity and volume; densities become similar to seawater.		turbulence, temperature and oil composition (presence of certain constituents which favor mousse formation)	P/VP
Photolysis	slow formation of oxygenated polar water soluble species which affect spreading and mousse formation and may contribute to the toxic burden of oil in water column	may become noticeable after a week or more	presence of sunlight/clouds, interrupted by nights	F/VP
Sedimentation	rarely expected through weathering alone in cold waters; temporary submergence in the top meters may occur in consequence of high seas and overwashing by waves; it may occur if oil associates with suspended matter		increased density as a result of weathering process; association with suspended particulate matter (SPM) or fecal pellets	F/P
Biodegradation	it may be the ultimate fate of much of the dissolved and dispersed oil	after ~3 months and may persist for years	hydrocarbon dilution and degradability; water contents of nutrient and oxygen; location of the spill (open sea versus coastal zone)	G/P

*The qualitative scale presented by Mackay & McAuliffe (1988) was used: F—Fair; G—Good; E—Excellent; P—Poor; VP—Very Poor.

oil without considering the dispersed oil remaining in the water column or sinking to the sea floor. The effect of wind and currents in the advection of the slick is also not taken in account.

The algorithms adopted in the present model were chosen to form a set of equations which could be written in the form of differential equations, making use of available oil parameters, which could reflect the interdependence of the processes. With this purpose, the evaporative exposure method was selected to model evaporative loss, since it requires information easily available from distillation data, and equation (9) is suitable to write in the differential form (equation (22)).

Equation (11) was used in the differential form to describe the incorporation of water into oil (equation (24)). Equation (3) was selected to compute the spreading area because it is suitable to include in the system of differential equations, and constant K_1 can be changed for calibration of spreading area.

In order to compute the viscosity increases, both mousse formation and evaporation processes were taken in account. Thus, the viscosity change is calculated as the sum of both the change on viscosity due to water incorporation and the change due to mass loss by evaporation. This was done by summing the right sides of equation (12) and equation (13) in differential form leading to equation (26).

A mass balance, or a volume balance, since it is referred to the initial surface oil and its initial density, is introduced in the system. Oil is allowed to escape from the surface slick by two processes which are the most important ones: evaporation from the surface and entrainment into the water column. Volume variation rate includes these two processes. Volume decrease by evaporation may be expressed by

$$V(t) = V_0 - \Delta F_E V_0$$

where V_0 is the initial spilled volume and $V(t)$ is the volume at time t . Dividing by Δt one obtains

$$\frac{\Delta V}{\Delta t} = -V_0 \frac{\Delta F_E}{\Delta t}$$

Taking the limit when $\Delta t \rightarrow 0$, equation (20) is obtained.

$$\frac{dV}{dt} = -V_0 \frac{dF_E}{dt} \quad (20)$$

If it is considered that the slick thickness h does not change during dt , which is a fair assumption for small time increments, variation of volume due to

entrainment into the water column may be expressed by

$$V(t + dt) = V(t) - D dt V(t),$$

since D is the fraction of sea surface lost by entrainment of surface oil into water column per hour given by equation (15), which corresponds to a fraction of volume lost per hour, if slick thickness remains constant. The volume variation rate obtained due to this process alone is

$$\frac{dV}{dt} = -DV \quad (21)$$

By taking the two effects simultaneously equation (23) is obtained.

The resulting system of differential equations is the following:

$$\frac{dF_E}{dt} = \frac{KA}{V_0} \exp \left(A - \frac{B}{T}(T_0 + T_G F_E) \right) \quad (22)$$

$$\frac{dV}{dt} = -V_0 \frac{dF_E}{dt} - DV \quad (23)$$

$$\frac{dY}{dt} = 2.0 \times 10^{-6} (W + 1)^2 \left(1 - \frac{Y}{C_3} \right) \quad (24)$$

$$\frac{dA}{dt} = K_1 A^{-1} V^{4/3} \quad (25)$$

$$\frac{d\mu}{dt} = C_4 \mu \frac{dF_E}{dt} + \frac{2.5\mu}{(1 - C_3 Y)^2} \frac{dY}{dt} \quad (26)$$

To solve the system of differential equations above the fourth-order, the Runge-Kutta method was used. The simulation process takes advantage of the fact that all the processes included in the system above share in common the characteristic that they show a greater variation in the beginning of the simulation, but the variation decreases as time proceeds. So, it is evident that the step size must be smaller in the beginning of simulation, but it can increase as time advances, reducing the time of simulation without losing precision. The spreading process ceases at some specified terminal thickness.

Numerical example

In order to test the results predicted by the proposed algorithm spills that could be compared with the limited amount of experimental data available were simulated. For this propose the experimental data from Buchanan & Hurford (1988) and from CONCAWE (1983) were considered here.

The crude parameters used are listed in Table 2. Values of 20 mN m^{-1} for the oil-water interfacial tension and 70% for the emulsion final water content, were used for all crudes, since no other values were available. The typical range for oil-water interfacial tension is $20\text{--}30 \text{ mN m}^{-1}$ and this parameter is reported not to be determinant in explaining differences in the rate of natural dispersion of various crudes (CONCAWE, 1983). A seawater with 35°S , with a density 1.024 g cm^{-3} (25°C) and a relative viscosity of 0.682 (the viscosity of pure water at 0°C is 1.787 cP) was used (Horne, 1969).

The mass transfer coefficient for evaporation was computed by the simplified formula (6). This formula gives good predictions of the order of magnitude of the mass transfer coefficient according to the values mentioned by Stiver & Mackay (1984), and it was considered to be good enough for our purposes.

Plots in Figs 3 and 4 concern evaporation alone and show that the shape of the evaporative loss curve is well predicted, but the agreement with experimental data is much better for large spills (in the order of $10\,000 \text{ m}^3$).

As stated in CONCAWE (1983) this may arise from the fact that for small spills processes like dispersion and emulsification, which compete with evaporation may become more important, and they are not included in calculation.

Plots in Figs 1 and 2 show that evaporation loss has a small increase with temperature and wind speed.

In Fig. 5 the evaporative loss curves of crudes with different volatility characteristics are compared with the corresponding ones presented in CONCAWE (1983). In fact the crudes chosen represent five

groups of different specific gravities. Reference to Table 2, which lists the densities of the different crudes and to Fig. 5, show that evaporation curves are distinguished by the densities of the crude oil, with the lighter crudes evaporating more than the heavier crudes. An exception is the Gamba crude which has a very high pour point (above $5\text{--}10^\circ\text{C}$).

In order to compare the curves obtained by the model and the curves shown in CONCAWE (1983) these curves are included in Fig. 5 (dotted lines). All the curves calculated show a greater increase in the fraction evaporated in the first hours after the spill compared with the curves from CONCAWE (1983), but later the agreement between the curves improves. Exceptions are the curves calculated for Gamba and Tia Juana Pesado crudes which show an overestimation in relation to the curves from CONCAWE during all the simulation. This behaviour is probably due to a greater computed decrease in slick thickness in the first hours of spill than the one computed by model used in CONCAWE (1983).

For the cases of Gamba and Tia Juana Pesado, these are crudes with high densities and with high pour points (respectively 33 and 3°C), which spread less than the other crudes. The model treats crudes independently of their pour points, so it is not surprising that the fraction evaporated is over-estimated, since the slick area for these crudes, should not increase as much as computed by the model.

In order to test the other processes only one case was simulated for which there was experimental data available on evaporative loss, water content, viscosity and density variation with time. That was a long term spill involving the release of 100 tons of Statfjord crude oil that was monitored over a period of seven days. The crude physical properties used are presented in the Table 2. The wind speed considered was 15 km h^{-1} and a temperature of 15°C was used. No data were available for these parameters, which are expected not to have a great influence in the results of simulation.

The plots in Fig. 6a for the evaporative curve show that the model over-estimates the whole evaporative

Table 2 Physical parameters for various crudes

Crude	Density (g cm^{-3})	Viscosity 40°C (cSt)	Evaporative Exposure Parameters*	
			T0 (K)	TG
Ekofisk	0.804	2.16	259	496
Statfjord	0.832	3.64	301	500
Forties	0.839	4.1	295	546
Gamba	0.868	21.7	375	666
Kuwait	0.870	10.3	294	636
Tia Juana Pesado	0.987	3730	439	970

*Evaporative exposure parameters were calculated by linear regression from data points of distillation curves (CONCAWE, 1983), which are assumed to be linear up to 250°C .

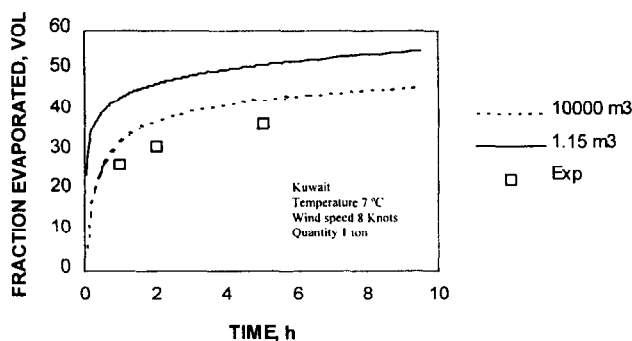


Fig. 3 Comparison of model predictions, for evaporation curves using different spilled volumes, with experimental data of CONCAWE (1983).

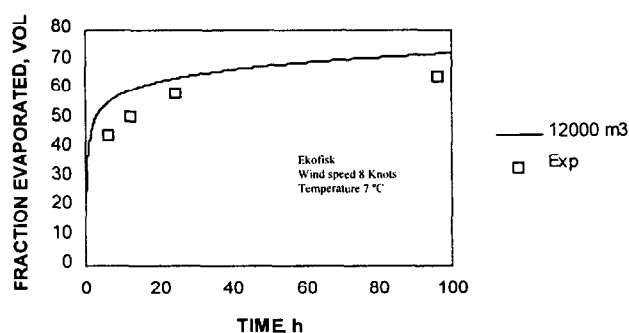


Fig. 4 Comparison of model predictions of evaporation curve for an oil spill of 12000 m³ with experimental data from CONCAWE (1983).

curve. The model results are within the values expected for Statfjord crude which is a fairly volatile crude and is expected to evaporate more than 50% in the first 24 h for a 10000 m³ spill (CONCAWE, 1983). One reason for model failure may be a scaling factor because most of the data used for model validation have been obtained for relatively small spills (≤ 20 m³). Another problem which concerns all highly volatile crudes is that distillation data are based on fresh crude but the oil spilt or evaporated for laboratory calibration may have already lost some of the highly volatile components. That would mean that

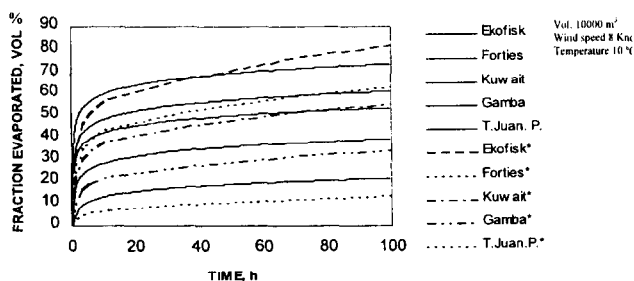


Fig. 5 Relationship between computed percentage of oil evaporated and time after spillage for different crude oils. Dotted lines are the curves calculated in CONCAWE (1983).

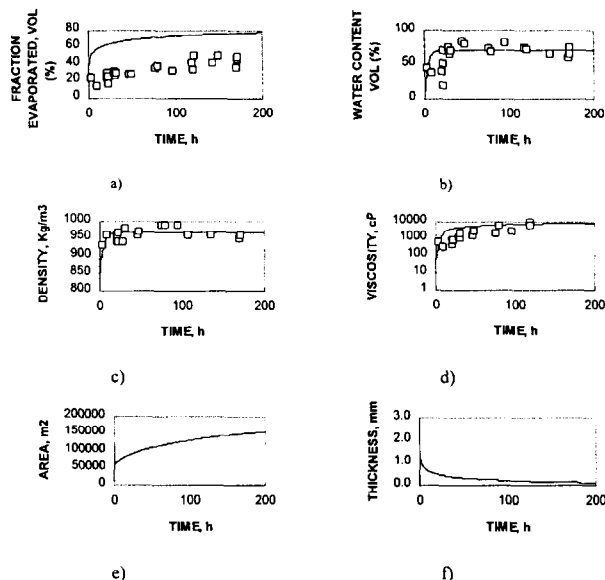


Fig. 6 Example of simulation of physicochemical properties of an oil spill of 100 t of Statfjord crude oil. The plots a-d have experimental points from Buchanan & Hurford, 1988. It was assumed a wind speed of 15 km h⁻¹ and a temperature of 15°C, since no data was available for these parameters.

low evaporative loss values would be determined (Buchanan & Hurford, 1988).

The water content curve, Fig. 6b, shows a good agreement between model predictions and experimental data, although it over-estimates the initial rate of water incorporation. This is probably due to variation in environmental conditions, particularly wind speed which was certainly not constant during the simulation.

The density curve predicted (Fig. 6c) shows a good agreement with experimental data.

In the case of viscosity, Fig. 6d, a fair agreement is found between the model and experimental data but an over-estimation is predicted during most of the spill. This prediction was obtained with a value of 5 for constant C_4 . If C_4 had a value of 10, which is the value reported in Spaulding *et al.* (1992) for crude oils then very high values were predicted for viscosity. This is probably due to the use of equation (26) which includes the effect of both evaporation and water incorporation in the calculation for viscosity.

The values of the area predicted are, according to the results reported by Lehr *et al.* (1984), underestimated (Fig. 6e). However the model allows the user to vary the constant K_1 for calibration of the computed value of area.

It can be concluded that the algorithm reproduces satisfactorily the results by other authors, although more experimental data are still needed for a better validation, particularly for the entrainment algorithm. The advantage of using a simulation instead of computing the variation of each process indepen-

dently is that the simulation should become more realistic and the environmental conditions are allowed to vary during simulation, namely the wind speed. A better agreement was expected with experimental data because, for instance, slick thickness is allowed to decrease along the simulation, and that should slightly improve the estimation of the fraction evaporated. However no evidence of better results was found and an over-estimation of the evaporation curves seemed to occur.

Conclusions

A review was provided of the main mechanisms that affect the fate of oil spills at sea. For each mechanism different expressions have been proposed which model the main phenomena present as a function both of physical variables and of empirical factor.

A model was proposed to represent the fate of oil spills as a result of the coupled action of the various mechanisms. This was represented by a set of differential equations that were solved numerically.

The comparisons of the model predictions with the scarce experimental data available, were satisfactory and the model predictions are more realistic than computing the effect of each process separately as done by some authors, since in this way the interactions between the processes are accounted for.

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